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CHARACTERIZATION, BENEFICIATION, AND REES EXTRACTION OF COAL BOTTOM ASH

KARAKTERISASI, BENEFISIASI, DAN EKSTRAKSI LOGAM TANAH JARANG DARI ABU BATUBARA DASAR

ISYATUN RODLIYAH[1], SITI ROCHANI[2*], SARIMAN[2], SUGANAL[2],
DATIN F. UMAR[2], and PRAMUSANTO[3]

[1] Testing Center for Mineral and Coal *tek*MIRA
Jl. Jenderal Sudirman No. 623. Bandung. Indonesia 40211
[2] Geological Resources Research Center, National Research and Innovation Agency
Kampus BRIN Bandung, Jalan Sangkuriang no 21, Bandung, West Java, Indonesia 40135
[3] Bandung Islamic University
Jl. Tamansari No.1. Bandung. Indonesia 40116
* Corresponding author's e-mail: rochani2013@gmail.com

ABSTRACT

Rare earth elements are strategic materials. The elements have critical roles in meeting the needs of raw material for producing the modern industrial products. Most of the REE minerals is available in the form of associated minerals. One of them is coal. In terms of obtaining an overview regarding the possibility of coal to be a source of REEs, a research was carried out by beneficiating the bottom ash of the coal using a shaking table and a magnetic separator, and was followed by extracting the REEs using the alkaline fusion and leaching them using the nitric acid. The results showed that the bottom ash of gasified coal from the Palimanan pilot plant contained cerium, lanthanum, samarium, neodymium, praseodymium, europium, gadolinium, dysprosium, and yttrium, with a total content of 77.85 ppm. Concentrating the REEs using the shaking table and the magnetic separator result in a recovery of 32.96% and 50.5%, respectively. Extracting the REEs by alkaline fusion using NaOH as flux was not promising while leaching with nitric acid was able to extract the REEs with various percentage extraction values, and the highest extraction for Neodymium was 73.46% under conditions of 2M nitric acid leaching and heated at 80°C.

Keywords: beneficiation, coal bottom ash, nitric acid leaching, rare earth elements.

ABSTRAK

Logam tanah jarang (LTJ) adalah logam strategis yang sangat penting. Logam tersebut memiliki peran dalam memenuhi kebutuhan bahan baku untuk produk industri modern. Keberadaan mineral LTJ sebagian besar berupa mineral ikutan, salah satunya adalah batubara. Untuk mendapatkan gambaran kemungkinan batubara menjadi sumber LTJ, telah dilakukan penelitian dengan memanfaatkan abu dasar batubara menggunakan meja goyang dan pemisah magnetik dan dilanjutkan dengan ekstraksi LTJ secara fusi basa dan pelindian menggunakan asam nitrat. Hasil penelitian menunjukkan bahwa abu dasar batubara hasil gasifikasi dari pilot plant *Palimanan mengandung serium, Lantanum, Samarium, Neodimium, Praseodimium, Euporium, Gadolinium, Disprosium, dan Itrium dengan total kandungan 77,85 ppm. Proses pengkonsentrasian LTJ dengan meja goyang dan pemisah magnetik menghasilkan perolehan masing-masing 32,96% dan 50,5%. Ekstraksi LTJ secara fusi basa menggunakan NaOH sebagai fluks tidak menjanjikan, sedangkan pelindian dengan asam nitrat mampu mengekstraksi LTJ dengan berbagai persentase nilai ekstraksi. Ekstraksi tertinggi untuk neodimium adalah 73,46% pada kondisi pelindian dengan asam nitrat 2M dan dipanaskan. pada 80 °C.*

Kata kunci: abu dasar batubara, benefisiasi, logam tanah jarang, pencucian asam nitrat.

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INTRODUCTION

Nowadays, the rare earth elements (REE) contribute a significant role to fulfill the needs of modern industries; for example: materials in the manufacture of superconductors, lasers, electronic optics, computer memory, DVDs, rechargeable batteries, LED and iPad applications, cell phones, catalytic converters, magnets, fluorescent lamps, and ceramics. The REEs are called strategic materials. Several large countries, such as European Union United States, have determined the rare earth metals as their critical materials and have the highest supply risk value (Gielen and Lyons, 2022). In general, the rare earth metals are primarily found in Monazite, Xenotime, and Bastnasite, but these rare earth metals also are found in mineral associates in small amounts, including coal (Harrar *et al.*, 2022).

Coal gasification is a chemical conversion process from coal in the form of particles or solids to gas with a combustible value. Coal gasification is a partial oxidation reaction of coal with oxygen or air. In addition, to produce the gas that has a calorific value, this gasification also produces a by-product in the form of ash because the process is carried out at temperatures below the melting point of coal, so it does not melt to form a material such as glassy slag which is inert and able to interfere in the form of a floated layer or clog the bottom of the gasifier.

Studying the rare earth metals in coal ash, it is stated that the coal ash could be a source of rare earth elements and categorized as a strategic mineral (Mayfield and Lewis, 2013; Franus, Wiatros-Motyka and Wdowin, 2015; Woźniak and Gurdziel, 2021). Suganal, Umar and Mamby (2018) identified the rare earth metal content in the coal bottom ash from steam power plants containing Cerium, Lanthanum, Yttrium, Neodymium, and Samarium less than 100 mg/kg. Park *et al.* (2021) found that the bottom and fly ashes contained 185.8 mg/kg and 179.2 mg/kg of REEs, respectively. Rao *et al.* (2021) stated that the fly ash from a lignite coal-based power plant located in Southern India contains total Rare Earth Elements in the range of 2100 mg/kg. Pan *et al.* (2018) studied the characteristic of REEs in coal fly ash from Guizhou Province, China using a particle size analysis, a sequential chemical extraction, and a scanning electron microscope. The relationship between the content of REEs and particle size was confirmed with previous results and implies that the particle separation can be used to enrich the chemical extraction of REEs from the coal fly ash.

REEs extraction from coal fly ash by acid leaching has been carried out (Peelman *et al.*, 2014). Kashiwakura *et al.* (2013) used dilute sulfuric acid (H_2SO_4), a leaching condition at temperatures of 30 to 80°C for 120 minutes. The results were not promising with the highest leaching recovery rate at 45% and the lowest around 8%. While Honaker, Zhang and Werner (2019) that used dilute chloric acid (HCl) to extract the REEs from coal ash found the recoveries of REEs up to ~80% for all the coal sources. Peiravi *et al.* (2017) developed a suitable flow sheet for REEs from coal ash with the highest REEs concentration of more than 700 ppm at high-temperature leaching with nitric acid, followed by solvent extraction tests using various organic extractants. The highest recovery rates of 90% for light rare earth elements (LREE) and 94 % for heavy rare earth elements (HREE) were obtained in the optimum leaching test conditions while maintaining impurity recovery to the leachate at less than 40%. Di 2 Ethyl Hexyl Phosphoric Acid (D2EHPA) was the best extractant in the solvent extraction test series, providing an REE recovery rate of almost 99%. Development of sequential chemical roasting, water washing, and acid washing processes to recover REEs from coal fly ash (Pan *et al.*, 2021). The Patent invention describes a method to extract REEs from selected coal combustion fly ashes using mild inorganic acids at ambient temperatures via a thREEs-step mild acid extraction process that results in high contents of extraction (ranging from 80-100%) (Stuckman, Lopano and Tarka, 2020). While Wang *et al.* (2019) used hydrofluoric acid (HF) for the extraction. alkali fusion using extraction REEs. Tang *et al.* (2019) studied to enrich and extract the REEs using alkali fusion-acid leaching. It was roasted at high temperature with Na_2CO_3 addition, followed by the leaching step. The optimum conditions of alkali fusion were 1:1 (mass ratio of Ash/Na_2CO_3), heating at 860 °C for 0.5 h. Optimal operating conditions with leaching time (2 hours), stirring speed (400rpm), and HCl concentration (3mol/L) resulted in 72.78% REEs leaching efficiency and the solid-liquid ratio (1/20). In another paper, Tang *et al.* (2022) used a coal fly ash sample and five REEs, namely Y, La, Ce, Pr, and Nd, in the sample as objects. The mechanism of alkali fusion processes of coal fly ash with different alkali fluxes (Na_2CO_3, NaCl, Na_2O_2, NaOH, KOH, and $Ca(OH)_2$) was studied.

Investigation of REEs sources other than coal ash was studied, such as industrial biomass and peat fly ash (Perämäki, 2014). This paper aimed to find new sources for REEs apart from its minerals such as monazite, bastnasite, etc. (de Vasconcellos *et al.*, 2006; Peelman *et al.*, 2014).

This paper's aim is to identify, beneficiate and extract the REEs from coal bottom ash as the gasification waste process by leaching the ash on nitric acid to find the efficient process to obtaining the REE sources other than its minerals.

METHODS

Preparation of Coal Bottom Ash Samples

The size of the coal bottom ash obtained from coal gasification pilot plant was reduced to -40 mesh using a disk mill and -100 mesh using a ball mill. Initial analyses the comprised of proximate, ultimate, ash composition, and X-Ray Diffraction (XRD) used an ash at size of -40 mesh. Meanwhile, the ash of -100 mesh size was used for analysis by Scanning Electron Microscope (SEM) and Inductively Coupled Plasma (ICP) and to be used as raw material for further beneficiation processed to upgrade the REEs contents using shaking table and magnetic separator.

Beneficiation

The prepared samples were upgrade in two stages:

1. Separation with differences in density was carried out using shaking table to produce concentrated, middling, and tailing products. The REE fractions were dried in an oven then each fraction was sampled for analysis the REEs contents using ICP.
2. Separating with different magnetic properties using a magnetic separator (5,000 Gauss) results in the products in the form of magnetic and non-magnetic fractions. Each fraction was sampled and then analyzed using ICP.

Leaching

The fraction was selected based on the highest REEs content and analyzed using the ICP, the Atomic Absorption Spectroscopy (AAS), and the XRD to determine the types of minerals.

a) Samples were melted by alkali (alkali fusion) using sodium hydroxide and dissolved in water. The solution and precipitate were analyzed using the ICP.
b) The selected samples were leached using nitric acid using two variables: temperature of 70, 80, and 90°C and acid concentrations of 1M, 1.5M, and 2M. The leaching solutions and precipitates were then analyzed using ICP.

The metal extraction was calculated by comparing the extracted metal weight in the solution/precipitate (W_t) to the initial weight (W_i) of the sample

$$\%\ \text{element extraction} = \frac{W_t}{W_i} \times 100 \quad \text{..............(1)}$$

RESULTS AND DISCUSSION

Bulk Sample Analysis

Table 1 indicates the analytical results of the coal bottom ash. It contained 39.57% fixed carbon instead of 51.24% ash. Physically, the color was black. XRD analyzed the mineral composition of the ash. The results showed that significant minerals were silica (SiO_2), silica hydrate ($SiO_2.xH_2O$), magnetite (Fe_3O_4), aluminum silicate ($Al_6Si_2O_{13}$), albite (feldspar mineral) ($NaAlSi_3O_8$), and hematite (Fe_2O_3). While analysis using SEM X-Ray Mapping can be seen in Table 2 and Figure 1. It contained 58.26 % C, while the REE content showed 0.01 % Nd_6O_{12} and 0.39 % Eu_2O_3.

Table 1. Characteristics of the coal

Proximate	% ADB	Ultimate	Percentage (% ADB)
Moisture	4.57	Total Sulfur	0.27
Ash	51.24	Carbon	42.37
Volatile matter	4.62	Hydrogen	0.94
Fixed Carbon	39.57	Nitrogen	0.22
		Oxygen	4.96

Table 2. Compounds in coal bottom ash from SEM X-Ray Mapping analysis

No.	Compound Name	Mass (%)
1	C	58.26
2	Al_2O_3	13.40
3	SiO_2	16.02
4	P_2O_5	1.23
5	CaO	3.19
6	FeO	7.50
7	Nd_6O_{12}	0.01
8	Eu_2O_3	0.39

The x-ray mapping results detected the elements C, O, Al, Si, P, Fe, Ca, Eu, and Nd. It can be seen that the elements C, O, Al, and Si are scattered in high quantities, indicated by a solid red color in the image of the distribution of elements (Figure 1). The detected elements bind/associate with each other, as for the elements Eu and Nd, which have very minimal quantities, indicated by the color of the distribution of elements that are not concentrated/not pink. In detecting each of the ash element's contents, AAS principal elemental composition analysis is shown, while ICP carries out the REEs content. The analysis results show in Table 3. Silica is the highest content, followed by alumina and iron oxide. While REEs content was dominated by Cerium, Yttrium, Lanthanum, and Samarium, it also contained Neodymium and Praseodymium as it is known that the two elements have higher prices compared to the other REEs, and these elements are used as raw materials for permanent magnet. The total of REEs was 77.85 ppm.

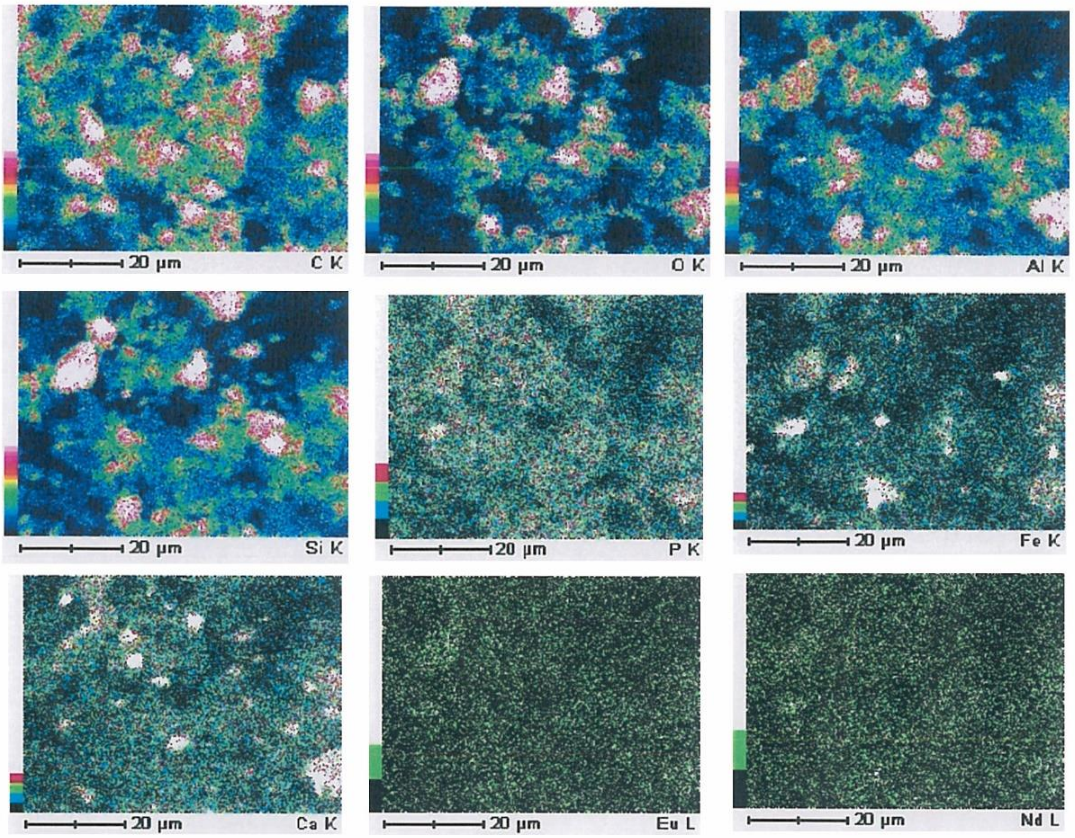

Figure 1. Mapping results of the elements contained in the coal bottom ash

Table 3. The composition of the coal bottom ash

No.	Compound	Mass (%) AAS
1	SiO_2	47.96
2	Al_2O_3	30.33
3	Fe_2O_3	8.87
4	K_2O	0.70
5	Na_2O	0.95
6	CaO	6.92
7	MgO	1.88
8	TiO_2	1.19
9	MnO	0.029
10	P_2O_5	0.60
11	SO_3	0.36
No.	**Element**	**Level (ppm) ICP**
12	H_2O	0.009
13	Ce	16.35
14	La	11.13
15	Sm	9.13
16	Nd	6.97
17	Pr	7.66
18	Eu	2.16
19	Gd	7.60
20	Dy	4.54
21	Y	12.27
Total REE		**77.85**

This composition analysis results would then be used to determine the upgrading process stages' extraction efficiency.

Beneficiation

Upgrading process using shaking table

The assay was carried out to separate the REEs from other impurities by their density differences. The 5,000 g feed yielded 680.45 g concentrates, 87 g middlings, and 1,172 g tailings. It was figured that the lost weight during the processing was due to the sample size, which was 100 mesh or 74 microns. According to Wills (2006), particle sizes suitable for processes using a shaking table were 100 - 700 microns or 140 - 25 mesh. Later, the REEs fractions were analyzed using ICP to determine the distribution of REE after the processing. The REE contents can be seen in Table 4.

Table 4. REE contents after the tabling process

No.	Metal	REE contents (ppm)		
		Concentrate	Middling	Tailing
1	Ce	35.31	26.22	16.11
2	La	32.20	27.00	14.76
3	Sm	23.17	15.32	13.55
4	Nd	15.63	4.35	9.39
5	Pr	23.86	16.84	10.35
6	Eu	3.14	1.32	2.00
7	Gd	19.22	15.67	9.65
8	Dy	13.44	8.13	3.74
9	Y	22.52	22.49	14.43
Total REE		**188.54**	**137.38**	**94.03**

Separation with density differences aimed to reduce the amount of silica and alumina in the ash. This process was chosen due to the REEs density between 4–8.5 g/cm^3, while silica density at 2.65 g/cm^3 and alumina at 3.95 g/cm^3. Therefore it was expected that the silica and the alumina would be concentrated in the tailing while the rare earth metals would be concentrated in the concentrate. After processing, the total REE in the REEs fractions was 419.95 ppm, and the ash was 77.85 ppm. Even though the REE still spread in the tailing and middling, the REE with the highest contents was in the concentrate (188.54 ppm). The recovery of each element's contents can be seen in Figure 2.

Recovery the REEs in the middling has the smallest value due to the small content as well as the weight of the fraction. In the concentrate, the highest recovery metal was Praseodymium which was 42.37%, followed by Dysprosium (10.3%) and Lanthanum (39,95). While in the tailings, the metal with the highest recovery was Sm 34.77%. Based on the classification of rare earth metals by weight, the 9 REEs included in the heavy rare earth metals group are Gadolinium, Dysprosium, and Yttrium. It can be seen in Figure 2 that Gadolinium and Dysprosium metals were found mainly in the concentrate due to the relatively large densities of Gadolinium and Dysprosium, namely 7.59 g/cm^3 and 8.54 g/cm^3. As for Yttrium, although it is classified in the heavy rare earth metals group, the Yttrium density is smaller than that of the REE in the light rare earth metal group namely 4.47 g/cm^3 causes the Yttrium to be concentrated in similar recoveries in the tailing and the concentrate. In this case also occurred to Samarium, Neodymium, and Europium.

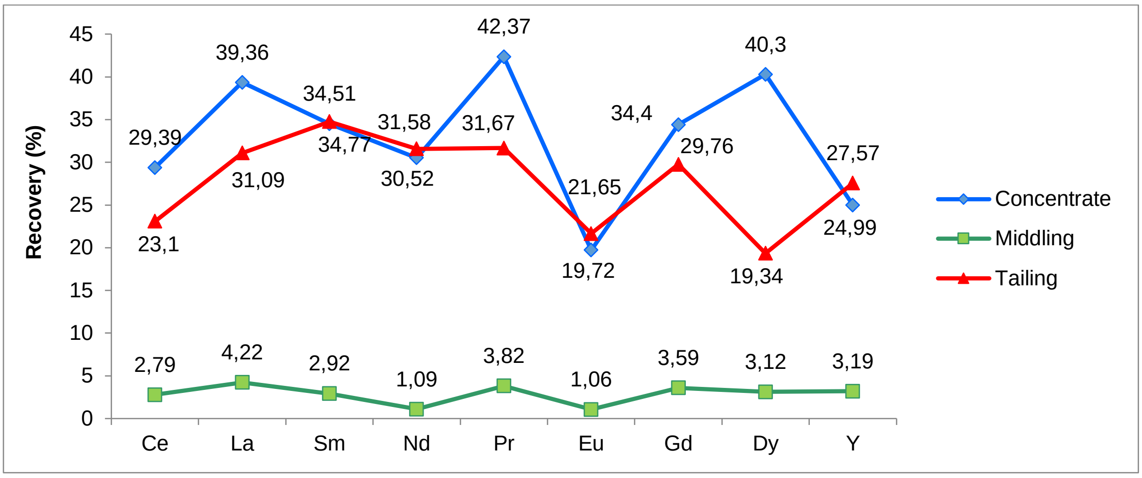

Figure 2. Tabling recovery chart for each metal

In contrast, although Cerium, Lanthanum, and Praseodymium are classified as the light rare earth metals group, they were mostly found in the concentrate because the REEs have relatively large densities, namely 6.77, 6.16, and 6.77 g/cm^3, respectively. The REEs recovery in Figure 2 reflects that metals with a density less than 6 g/cm^3 would be concentrated in the tailing, and those with more than 6 g/cm^3 tend to be found in the concentrate.

Upgrading process using a magnetic separator

A magnetic separator was processed to separate magnetic materials (paramagnetic/ ferromagnetic or magnets can attract that) and non-magnetic materials (diamagnetic or not affected by magnetic fields). The concentrate and tailing of tabling products were processed using a magnetic separator, while the middling cannot be further processed due to the small amount of the product. The REEs concentration after processing can be seen in Table 5.

This process was carried out using a magnetic separator. It was expected that the REEs would be attracted by the magnetic drum and accumulate in the magnetic fraction. While the impurities in the form of silica and alumina, which are non-magnetic, accumulated in the non-magnetic fraction. However, It was found that REEs are more concentrated in non-magnetic concentrate instead of magnetic concentrate. This was due to its minerals tending to accumulate into a non-magnetic fraction. While the total of REEs contents was 576.01 ppm, it was higher than in the shaking table process. The material lost due to magnetic processing was 1.96%. Figure 3 shows the recovery of each element.

Table 5. REEs contents after magnetic processing

No.	Element	Content (ppm)			
		Concentrate		Tailing	
		Magnetic	Non-magnetic	Magnetic	Non-magnetic
1	Ce	34.26	35.96	17.70	16.21
2	La	28.11	33.32	14.78	15.46
3	Sm	21.13	26.51	14.13	11.51
4	Nd	13.01	20.88	9.87	9.91
5	Pr	18.76	25.65	10.50	10.51
6	Eu	4.16	7.87	1.09	3.43
7	Gd	15.33	28.50	9.96	8.48
8	Dy	15.47	17.17	1.76	5.29
9	Y	18.97	21.31	15.83	13.05
Total REE		**169.25**	**217.22**	**95.66**	**93.88**

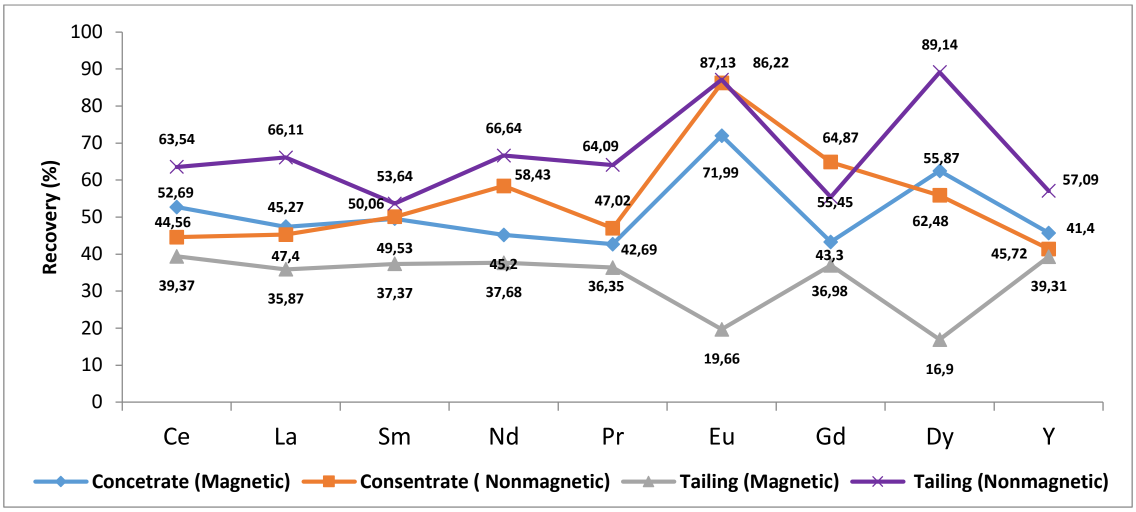

Figure 3. Graph of recovery resulting of the magnetic process (ppm)

In general, the non-magnetic fraction has a higher recovery than the magnetic fraction for most REEs. This occurred due to the REE in the coal bottom ash combined with the zirconium silicate ($ZrSiO_4$), a non-magnetic material. The REE was also bound to silica since it is not affected by magnets. Due to the influence of these silica bonds, many rare earth minerals are paramagnetic (slightly attracted by magnets). In the non-magnetic tailings fraction, dysprosium was the highest recovery (89.14%) in the non-magnetic concentrate fraction, and europium was the highest recovery (86.22%).

Figure 3 shows that for the magnetic process, the REEs in tailings was easier to separate compared to the REEs in the concentrate and the REEs recovery in the non-magnetic fraction was higher than that in the magnetic fraction. As the concentrate, magnetic processing could not separate the REE and the impurities very well, and this is shown in Figure 3 that the recovery values almost overlap each other, It means that the recoveries of REEs in the concentrates in either the magnetic and non-magnetic fractions are almost the same.

Although Figure 3 shows the non-magnetic tailings fraction that has the highest recoveries, in terms of REEs this fraction contained fewer REEs than the magnetic concentrate fraction. Therefore the next process, the magnetic concentrate, would be used for leaching experiments.

Leaching

Alkaline fusion process

Silica content in the ash can be reduced using the usual fusion process by dissolving sodium hydroxide dissolved in water. The results of the alkaline fusion can be seen in Table 6. In this experiment, sodium hydroxide was used as a flux.

The reaction occurred was as follows:

$REE_2(SiO_3)_3\ (s) + 3NaOH\ (s) \rightarrow REE(OH)_3(s) + 3Na_2SiO_3\ (s)$ .... (2)

$Na_2SiO_3\ (s) + H_2O\ (aq) \rightarrow Na_2SiO_3\ (aq)$ ... (3)

Table 6. REE content in the alkaline fused solution

Metal	REE contents (ppm)			
	AF1	AF2	AF3	AF4
Ce	0.1303	0.1043	0.1121	0.1084
La	0.0794	-	0.0798	-
Sm	0.0277	0.0004	-	-
Nd	0.014	-	-	-
Pr	0.0404	0.0094	-	0.0147
Eu	0.0354	0.0046	0.0006	-
Gd	0.0334	0.004	-	-
Dy	0.0743	0.041	0.0436	0.043
Y	0.0281	0.0045	0.0009	-
Total REE	0.463	0.1682	0.237	0.1661

Note: – is undetected

The alkaline fusion process was done to reduce the silica and aluminum contents. The analysis showed that the silica content decreased from 53.25% to 30.43% and the aluminum content from 30.73% to 22.5%. It seemed that the process could not delete silica and alumina completely. The fused products were dissolved in water and filtrated, and the filtrate was analyzed using ICP, as shown in Table 6.

Results of the alkali fusion process were not promising, it showed that the REEs content was minimal in the solution. This is probably caused by the sample being insoluble in the alkaline fusion process; thus, the REEs remains in the precipitate. In contrast to the results of the study by Tang *et al.* (2019) using Na_2CO_3 as flux and showed that 72.78% leaching efficiency was obtained in optimal operating conditions. It was mentioned that the results indicated that the alkaline fusion followed by the acid leaching method was favorable rather than a direct leaching method. Even different alkali fluxes (Na_2CO_3, NaCl, Na_2O_2, NaOH, KOH, and $Ca(OH)_2$) could be used for the extraction (Tang *et al.*, 2019).

Leaching process using nitric acid

The leaching process was carried out using a nitric acid solution. Experiments were carried out using variations in temperature and concentration of nitric acid. The leaching results can be seen in Table 7. The nitric acid here played a role in dissolving rare earth metals into the liquid phase. The process that occurred was as follows:

$REE(OH)_3\ (s) + HNO_3\ (aq) \rightarrow REE\ NO_3\ (aq) + 3H_2O\ (aq)$ ....(4)

REE content of the leached product was analyzed using ICP. The contents of REE can be seen in Figure 4.

Figure 5 to 7 shows that the REEs is not entirely extracting. It can be seen from the low extraction efficiencies.

The efficiency extractions at a temperature of 70°C (Figure 5) show that the highest average extraction efficiency occurred using nitric acid with a concentration of 2M. At each variation in nitric acid concentration at 70°C, the REEs element with the highest extraction efficiency was Neodymium (64.06%).

Figure 6 shows the extraction efficiency at 80°C, and the highest average extraction efficiency occurred using nitric acid with a concentration of 2M. The element with the highest extraction efficiency was Neodymium, with an extraction efficiency of 73.46%.

Figure 7 shows the extraction efficiency at 90°C, and the highest average extraction rate also occurred using a 2M concentration of nitric acid. Meanwhile, using a 2M concentration of nitric acid at 90 °C caused the recovery of some metals to decrease due to the other elements dissolved in nitric acid. At the 2M nitric acid heated at 90°C, the element with the highest extraction rate was Neodymium (69.38%).

Figure 8 shows the variable concentration of nitric acid and temperature plotted against the average REEs extraction efficiency. The best condition is using 2M nitric acid and heating at 80°C; it revealed that the higher the acid concentration was used, the higher the extraction rate obtained. It is due to the ability of the solvent to dissolve rare earth metals in the bottom ash of the coal. In addition, neodymium was the metal that was easier to be extracted.

Table 7. The results of dissolving the sample using nitric acid at different temperatures

Concentration nitric acid	70°C		80°C		90°C	
	Solution (ml)	Solid (g)	Solution (ml)	Solid (g)	Solution (ml)	Solid (g)
1 M	68	18.28	66	15.07	77	15.23
1.5M	46	15.7	50	15.98	72	16.14
2M	53	15.05	57	14.6	54	15.34

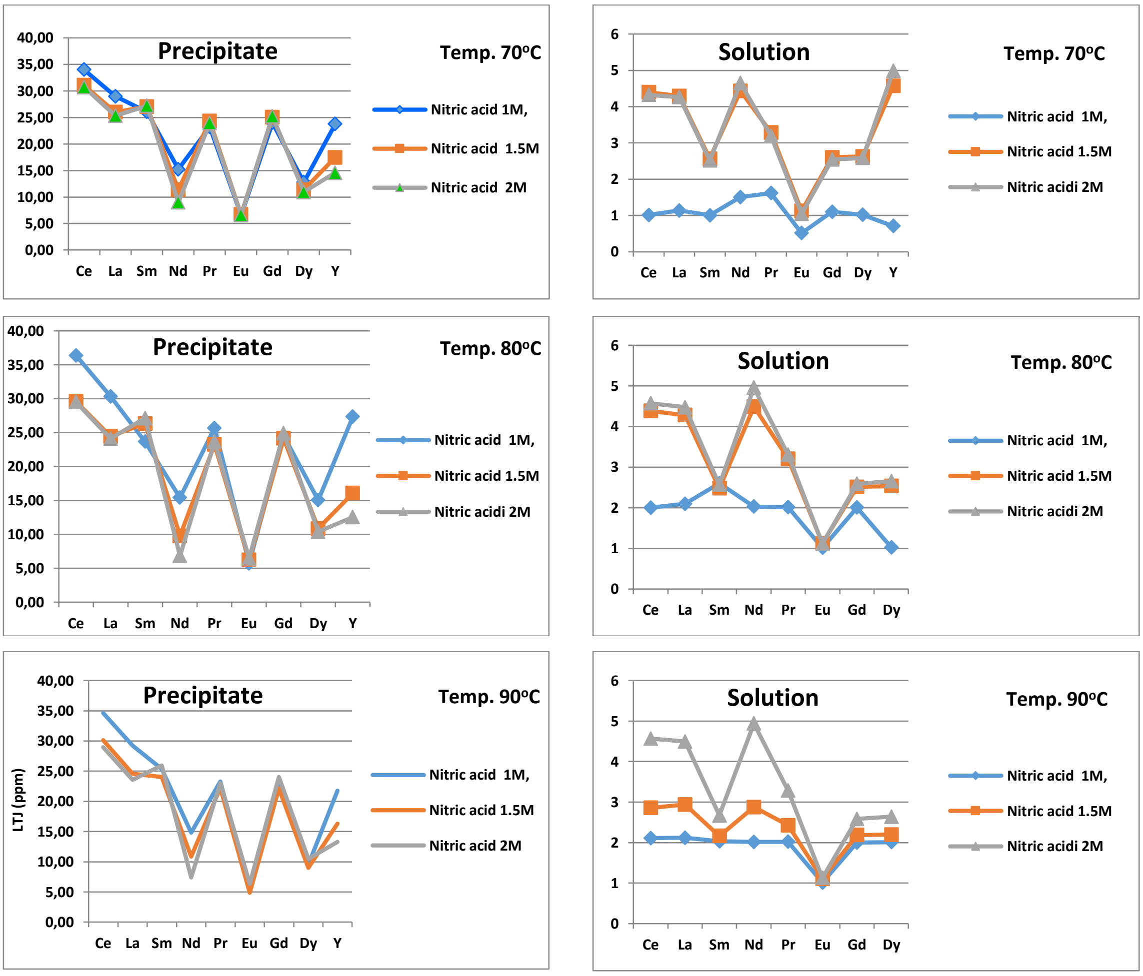

Figure 4. REE content in precipitates and solutions at various concentrations of nitric acid and temperature (ppm)

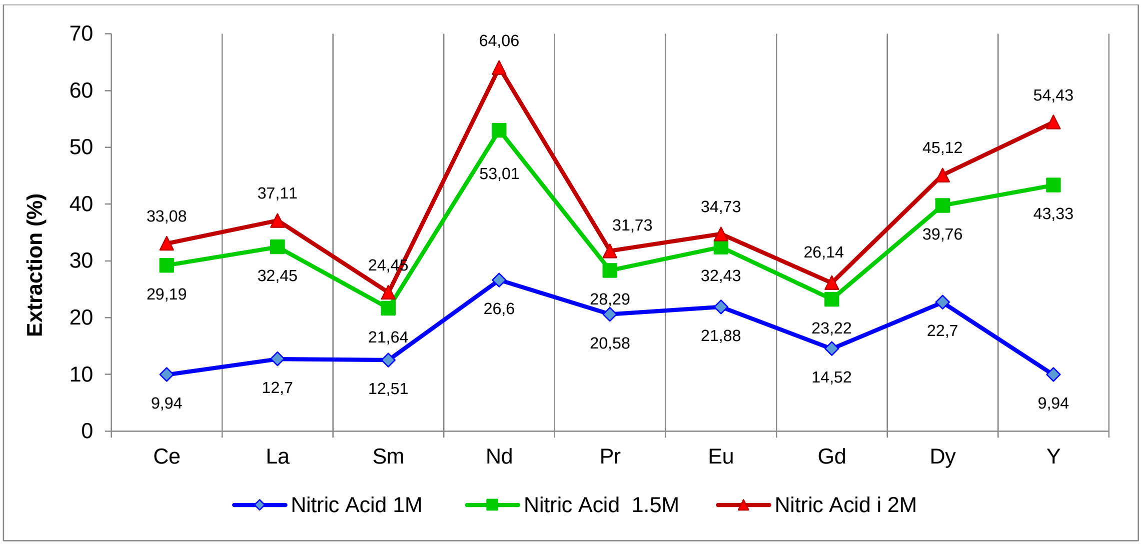

Figure 5. Graph of rare earth extraction efficiency at 70°C

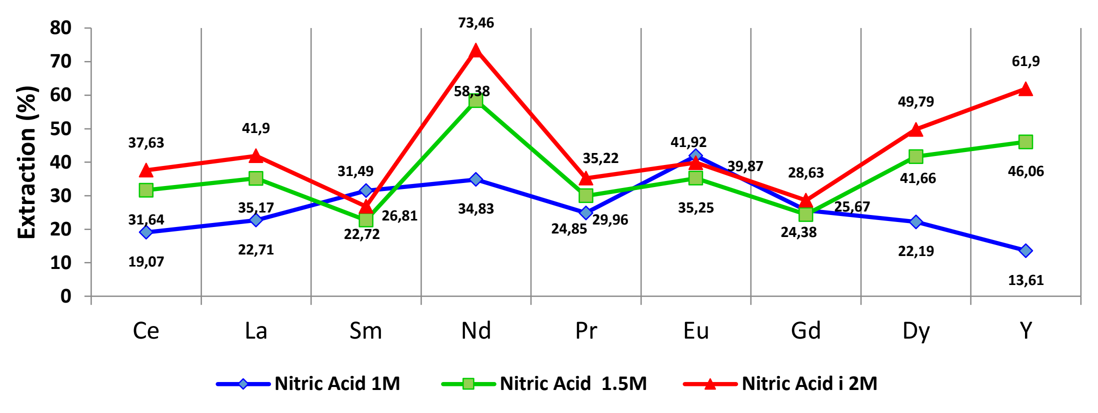

Figure 6. Graph of rare earth extraction efficiency at 80°C

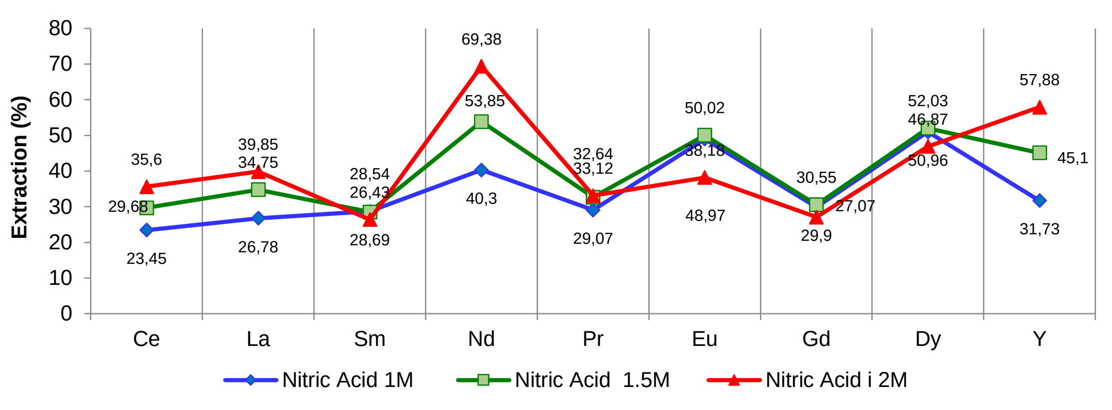

Figure 7. Graphs of Rare Earth Metal Extraction Efficiencies at 90°C

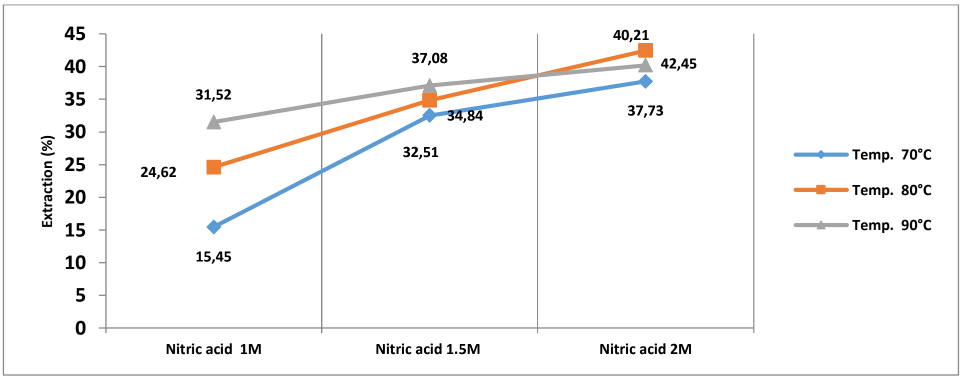

Figure 8. The efficiency extraction at variable temperatures and nitric acid concentration

The highest average extraction efficiency was 42.45%. It seemed that the extraction yield recovery was relatively low. The extraction is suggested, followed by solvent extraction using various organic extractants as Peiravi *et al.* (2017) accomplished. Similarly, the study by Kashiwakura *et al.* (2013) used dilute sulfuric acid (H_2SO_4) to extract REEs from coal ash, leaching at 30 to 80°C for 120 minutes. With the highest recovery rate at 45%. In contrast, Honaker, Zhang and Werner (2019) use dilute chloric acid (HCl) with a recovery of up to ~80% for all the coal sources.

Several rare earth elements, such as Praseodymium, Neodymium, Europium, and Dysprosium have high value and these elements should have an essential role in industries and can be counted as the added value of gasified coal fly ash. Some elements, such as neodymium and gadolinium could be used as supporting materials for renewable energy (as a permanent magnet) and as a contrast agent for MRI, respectively. Generally, this potential would assist the Indonesian government towards zero waste on coal utilization.

CONCLUSIONS

The total content of REEs in the coal bottom ash was 77.85 %. Beneficiation of REE contents using the shaking table resulted in low recovery in concentrate; however, there was an increase in the number of REEs to 419.95 ppm. While the following process was upgraded using the magnetic separator with a recovery of 50.4%, and the total REE increased to 576.03 ppm, the highest content in the non-magnetic concentrate fraction. The alkaline fusion process could reduce the silica and alumina, but the REEs extraction was not promising. The leaching process using 2M nitric acids and heated at 80°C resulted in the highest extraction efficiency for Neodymium of 73.46%.

The content of REEs in coal bottom ash should be a concern because of the abundant potential for coal ash from the combustion of Steam Power Plants. The demand for REE increases with the development of advanced materials-based industries. Currently, the production of REE is controlled by one country; therefore, it has become a critical material for several significant countries worldwide

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REFERENCES

Franus, W., Wiatros-Motyka, M. M. and Wdowin, M. (2015) ‘Coal fly ash as a resource for rare earth elements’, *Environmental Science and Pollution Research*, 22(12), pp. 9464–9474. doi: 10.1007/s11356-015-4111-9.

Gielen, D. and Lyons, M. (2022) *Critical materials for the energy transition: Rare earth elements*. Abu Dhabi.

Harrar, H., Eterigho-Ikelegbe, O., Modiga, A. and Bada, S. (2022) ‘Mineralogy and distribution of rare earth elements in the Waterberg coalfield high ash coals’, *Minerals Engineering*, 183, p. 107611. doi: 10.1016/j.mineng.2022.107611.

Honaker, R. Q., Zhang, W. and Werner, J. (2019) ‘Acid leaching of rare earth elements from coal and coal ash: Implications for using fluidized bed combustion to assist in the recovery of critical materials’, *Energy & Fuels*, 33(7), pp. 5971–5980. doi: 10.1021/acs.energyfuels.9b00295.

Kashiwakura, S., Kumagai, Y., Kubo, H. and Wagatsuma, K. (2013) ‘Dissolution of rare earth elements from coal fly ash particles in a dilute H2SO4 Solvent’, *Open Journal of Physical Chemistry*, 03(02), pp. 69–75. doi: 10.4236/ojpc.2013.32009.

Mayfield, D. B. and Lewis, A. S. (2013) ‘Environmental review of coal ash as a resource for rare earth and strategic elements’, in *2013 World of Coal Ash (WOCA) Conference*. Lexington: University of Kentucky Center for Applied Energy Research, p. 051.

Pan, J., Zhou, C., Liu, C., Tang, M., Cao, S., Hu, T., Ji, W., Luo, Y., Wen, M. and Zhang, N. (2018) ‘Modes of occurrence of rare earth elements in coal fly ash: A case study’, *Energy & Fuels*, 32(9), pp. 9738–9743. doi: 10.1021/acs.energyfuels.8b02052.

Pan, J., Hassas, B. V., Rezaee, M., Zhou, C. and Pisupati, S. V. (2021) ‘Recovery of rare earth elements from coal fly ash through sequential chemical roasting, water leaching, and acid leaching processes’, *Journal of Cleaner Production*, 284, p. 124725. doi: 10.1016/j.jclepro.2020.124725.

Park, S., Kim, M., Lim, Y., Yu, J., Chen, S., Woo, S. W., Yoon, S., Bae, S. and Kim, H. S. (2021) ‘Characterization of rare earth elements present in coal ash by sequential extraction’, *Journal of*

Hazardous Materials, 402, p. 123760. doi: 10.1016/j.jhazmat.2020.123760.

Peelman, S., Sun, Z. H. I., Sietsma, J. and Yang, Y. (2014) 'Leaching of rare earth elements: Past and present', in *1st European Rare Earth Resources Conference*. Milos: EURARE, pp. 446–456.

Peiravi, M., Ackah, L., Guru, R., Mohanty, M., Liu, J., Xu, B., Zhu, X. and Chen, L. (2017) 'Chemical extraction of rare earth elements from coal ash', *Minerals & Metallurgical Processing*, 34(4), pp. 170–177. doi: 10.19150/mmp.7856.

Perämäki, S. (2014) *Method development for determination and recovery of rare earth elements from industrial fly ash*. University of Jyväskylä.

Rao, K. A., Serajuddin, M., RamaDevi, G., Thakurta, S. G. and Sreenivas, T. (2021) 'On the characterization and leaching of rare earths from a coal fly ash of Indian origin', *Separation Science and Technology*, 56(3), pp. 541–557. doi: 10.1080/01496395.2020.1718705.

Stuckman, M., Lopano, C. and Tarka, T. (2020) 'US Patent pending: Step-leaching process of rare earth elements from select coal combustion fly ashes using mild inorganic acids at ambient conditions'. United Stated.

Suganal, Umar, D. F. and Mamby, H. E. (2018) 'Identifikasi keterdapatan unsur logam tanah jarang dalam abu batubara Pusat Listrik Tenaga Uap Ombilin, Sumatera Barat', *Jurnal Teknologi Mineral dan Batubara*, 14(2), pp. 111–125. doi: 10.30556/jtmb.Vol14.No2.2018.395.

Tang, M., Zhou, C., Pan, J., Zhang, N., Liu, C., Cao, S., Hu, T. and Ji, W. (2019) 'Study on extraction of rare earth elements from coal fly ash through alkali fusion – Acid leaching', *Minerals Engineering*, 136, pp. 36–42. doi: 10.1016/j.mineng.2019.01.027.

Tang, M., Zhou, C., Zhang, N., Pan, J., Cao, S., Hu, T., Ji, W., Wen, Z. and Nie, T. (2022) 'Extraction of rare earth elements from coal fly ash by alkali fusion–acid leaching: Mechanism analysis', *International Journal of Coal Preparation and Utilization*, 42(3), pp. 536–555. doi: 10.1080/19392699.2019.1623206.

de Vasconcellos, M. E., da Rocha, S. M. R., Pedreira, W. R., da S. Queiroz, C. A. and Abrão, A. (2006) 'Enrichment of yttrium from rare earth concentrate by ammonium carbonate leaching and peroxide precipitation', *Journal of Alloys and Compounds*, 418(1–2), pp. 200–203. doi: 10.1016/j.jallcom.2005.10.076.

Wang, Z., Dai, S., Zou, J., French, D. and Graham, I. T. (2019) 'Rare earth elements and yttrium in coal ash from the Luzhou power plant in Sichuan, Southwest China: Concentration, characterization and optimized extraction', *International Journal of Coal Geology*, 203, pp. 1–14. doi: 10.1016/j.coal.2019.01.001.

Wills, B. A. (2006) *Wills' mineral processing technology*. 7th Ed. Butterworth-Heinemann.

Woźniak, J. and Gurdziel, M. (2021) 'Rare earth elements in deposited hard coal fly ash in Poland', *E3S Web of Conferences*. Edited by S. Zhironkin et al., 278, p. 01016. doi: 10.1051/e3sconf/202127801016.